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Sampling Air for Gaseous Organic Chemicals Using Solid Adsorbents, Applications to Tenax

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SAMPLING AIR FOR GASEOUS ORGANIC CHEMICALS USING SOLID ADSORBENTS APPLICATION TO TENAX

by

Joseph F. Walling, Richard E. Berkley,
Donald H. Swanson, and Frank J. Toth
Pollutant Analysis Branch
Environmental Monitoring Division
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

A simple input-output model for a two phase flow system with fixed bed was applied to Tenax adsorption of atmospheric contaminants. The model fit laboratory data acceptably and relationships with previous approaches were stated. Chromatographic retention volumes are used in this model which provides a means of scaling adsorbent bed dimensions and flow rates to preserve desired output characteristics.

Suggestions are made about how to use the model for rational sampling design when quantitative information is needed. Practical limitations of field operations and fundamental knowledge and the need to evaluate every datum lead to practical suggestions for sampling. At least two samples collected simultaneously but at very different flow rates are suggested as necessary for quantitative work.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Toxic Substances and the Office of Enforcement.

This work is concerned with one kind of sampling technique which is currently used to collect trace organic chemical contaminants in the atmosphere. The topics of this report are a model of the sampling technique and its application to field operations.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina

ABSTRACT

Solid adsorbents are a convenient way to trap and concentrate trace atmospheric constituents. Loss of constituents of interest through exceeding the adsorbent capacity is always a problem and must be prevented if quantitative analyses are desired. Models currently applied to field sampling have been adapted from chromatography. They do not deal explicitly with the variables and decisions required in field sampling to avoid exceeding the adsorbent capacity. The goal of the present study was to test the application of an alternate model that would be useful in field work.

A simple input-output model for a two-phase flow system with a fixed bed was tested. The model parameters were adsorbent bed weight, dimensions, and flow rate and two parameters which characterize the chemical system and temperature. One of these was the familiar retention volume of chromatography. The other is a rate constant.

Experiments with chloroform, trichloroethylene, benzene and tetrachloroethylene were done using a permeation tube dilution system to simulate sampling with Tenax. Sampling tube output behavior was monitored using a flame ionization detector. Several substances were studied at two temperatures (50 and 100°F), several flow rates (35-500 cc/min), and differing bed weights and dimensions. The model described the situation well since retention volumes determined as a parameter of the model agreed well with literature values. The rate constant was less well characterized but it was sufficiently well behaved for present purposes.

This model permits scaling of cartridge dimensions and flow rates to preserve a desired output behavior. The model also facilitates practical flow rate calculations for sampling design. Limits of knowledge and information and practical considerations suggest that even when the model is applied it is necessary to take at least two samples simultaneously but at very different flow rates in order to assess whether adsorbent capacity has been exceeded. This work covers the period from March 1981 through April 1982 and work was completed as of September 1981.

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SECTION I

INTRODUCTION

Solid adsorbents are very convenient for use in field sampling and therefore have been employed extensively to concentrate trace organic pollutants in sampling ambient air prior to analysis. While solvent desorption followed by gas chromatographic analysis has been and continues to be used when charcoal is the adsorbent, more recently developed media such as Tenax employ thermal desorption of concentrated organics followed by a gas chromatography-mass spectrometry (GC/MS) analysis.

Typically when Tenax has been employed little or no reliable information about the content of the atmosphere has existed prior to the sampling. Usually the goal is to identify the organics present and possibly also to obtain quantitative information about several substances if they happen to be present.

Every Tenax sample taken is important because GC/MS analyses are very expensive. Moreover, each sample can be analyzed only once since the entire sample is used in the initial attempt at doing the GC/MS analysis. Therefore, strenuous efforts have been made in the past to insure competent sampling.

The fundamental problem in sampling is to avoid "significant" adsorbate loss during the sampling itself by not exceeding the capacity of the adsorbent for the material of interest. A common approach has been to assume that standard chromatographic theory could be applied to the adsorbing bed during the sampling. Usually, for substances which can be adsorbed nothing is observed in the output stream for some characteristic time after which increasing concentrations leak through the adsorbent bed until the output concentration is identical to the input concentration. At that point nothing more is adsorbed.

Unfortunately, cumbersome equations([1]) describe the output or leakage behavior of such chromatographic columns. Because of the complexity of the relationships, simplifying assumptions are invoked to construct practical guidelines regarding the maximum volume of air which can be sampled. These guidelines are accompanied by warnings about the non-trivial effects of other chemicals, temperature, and concentration on the retention volume and also of the flow rate and the number of theoretical plates on output behavior of any given adsorbent. The admonition to obtain appropriate information under conditions "comparable" to those likely to be encountered is always present in well written articles([1,2]).

Such an approach to the problem is impractical because basic information required by this approach is unavailable. For example, it is necessary to know before going to the field the kinds of organic species present, the approximate concentration ranges to be encountered, and the temperatures likely to be experienced during the sampling. Also, there is little likelihood of predicting sampling conditions since few data are available about the atmosphere.

Not surprisingly, an empirical approach to the problem has often been attempted. Usually an arbitrary flow rate has been selected and tandem tubes (two tubes attached in series) are employed. Both tubes must be analyzed before one piece of sampling information can be obtained; that is, two analyses are required and must be "combined" to give one datum about the atmosphere sampled. If the substance is found on the first tube but little or nothing is found on the second tube this is usually considered sufficient evidence of adequate retention of that substance by the first tube. If the substance is absent on the first tube also, it is usually interpreted to mean that the substance was not present.

If significant amounts of the substance are found on the second tube, often it is assumed that everything eluted from the first tube was collected and retained by the second tube. The total quantity of material in the sample is the sum of the amounts found on both tubes. It must be assumed that nothing significant eluted from the second tube. However, there is no practical way to check this assumption. Therefore, use of tandem tubes requires two analyses in order to get information about one sampling interval. Moreover, assumptions are still required in order to combine these two fragmentary pieces of information to give one datum for the sampling interval.

In some situations attempts have been made to "correct" data when the total air volume sampled exceeded an expected retention volume. Usually this is done when one cartridge has been used and results are needed for a variety of substances with different retention volumes. Such corrections invoke two extremely important unverifiable assumptions: (1) the sampling tube behaved as it would in frontal chromatography, (2) the retention (breakthrough) volumes determined chromatographically (probably in a chemically very simple environment under quite different fluid flow and temperature conditions) will be substantially correct at all times during the sampling.

Given these assumptions, the "correction" is done as follows: (1) one average, typical, effective, or perhaps extreme temperature is selected from the record of field sampling. The chromatographically determined retention volume for the substance of interest is estimated for the temperature chosen from available data. Retention volumes have significant temperature dependencies and sometimes, because of mechanistic changes, the temperature derivatives have some unpredictable discontinuities. (2) The "corrected concentration" is then computed using the relationship:

$$\frac{\text{(Volume Sampled) (ng found)}}{\text{(Retention Volume) (Volume Sampled)}} = \text{"corrected concentration"} \quad (1\text{-}1)$$

The equation states that only material collected in one retention volume will be retained. This "corrected result" assumes applicability in the field situation of the laboratory retention volume. The volume sampled plays no role whatever in calculating the concentration.

The best that can be done with the information about the field sample is to note that a correction of some kind is required and perhaps to estimate a factor which could approximate the time interval over which the corrected concentration might apply. If the ratio of the retention volume used to the total volume sampled were computed, this fraction of the sampling period from sampling termination backwards might be a reasonable time over which this concentration could be expected to have been present. Any application of that average number to the entire sampling interval would require additional assumptions which, again, cannot be verified.

For example, if the ratio of retention volume to total volume sampled were one-half and the sampling were done for 24 h, the result might be assumed to be applicable only to the last 12 h of sampling. If that quantity of material had, in fact, been sampled for the first 12 h it would have been eluting during the last 12 h. However, the assumption about the average value over the 24 h period would be correct.

On the other hand, assume that after the first 12 h the wind changed direction. Prior to the wind change none of the material of interest was sampled by the sampler. Then if the corrected concentration for that last 12 h sampling period were calculated by this procedure that value taken as the 24 h average would be larger by a factor of 2 than would have been observed if sampling could have been done properly for the entire 24 h period. Therefore, this approach makes it possible to obtain concentrations which are larger than the true average. This approach produces at best very expensive semi-quantitative indexes which are difficult to interpret and impossible to defend.

Since the main objectives of chromatography are not the same as those of field sampling with solid adsorbents, theory was not developed with the goal of solving the practical problems of establishing field sampling procedures. Variables which are critical in the field situation are not explicitly handled in a convenient way in chromatographic theory[1,2]. Moreover, applications of such relationships require a huge fundamental data base both prior to and subsequent to the field sampling. This is not practical for routine applications.

The objectives of this work, then, have been the following:

1. To obtain a simple approximate function incorporating a minimum number of adjustable parameters which establishes a relationship among important sampling variables:

(i) weight of adsorbent;
(ii) adsorbent bed (sampling tube) geometry;
(iii) flow rate;
(iv) input concentration to the adsorbent bed;
(v) adsorbent bed output concentration;
(vi) elapsed sampling time.

2. To test the accuracy of the function obtained in describing experience in a few simplified and controlled laboratory situations.

3. To assess the usefulness of this function for describing sampling behavior based on limited evidence.

4. To design a scheme for sampling and data interpretation that is sufficiently simple to be practical but which can provide evidence of consistency in the results from every sampling situation.

The remainder of this paper will present a simple functional model, describe the very limited testing done on it, and outline how it might be used to permit rational design of field studies without prior knowledge of the sampling conditions or a huge fundamental data base while providing an indication of consistency of resulting data. However, this approach will not guarantee that data obtained are accurate or complete nor can it guarantee even when properly applied that valid information will result. It can indicate the lack of consistency but will not provide the means to correct faulty information in that instance.

SECTION 2

THE SAMPLING MODEL

The simplest mathematical description of the input-output behavior of a two-phase system with a fixed bed and interphase adsorption when approached from the standpoint of a general mass balance([3]) is:

$$\ln \frac{C}{C_o} = \frac{K_o L}{V_L}\left[\frac{t}{t_s} - 1\right] \qquad (2.1)$$

Where C is the bed's exit concentration at elapsed time t, g/cm^3

C_o is the bed inlet concentration, g/cm^3

K_o is a pseudo first order rate constant, min^{-1}

L is the adsorbent bed length, cm

V_L is a superficial flow velocity, $\frac{\text{flow rate}}{\text{cross-sectional area}}$

For cylindrical reactors,

$$V_L = \frac{Q}{\pi R^2}, \frac{cm}{min} \qquad (2.1A)$$

where Q = volumetric flow rate, cm^3/min

R = bed radius, cm

t is the elapsed time after beginning of sampling, min

t_s is the elapsed time required to reach the adsorbing capacity of the bed. It is a ratio of the total capacity of a given bed to the rate at which adsorbate is brought to the bed:

$$t_s = \frac{W_s W}{Q C_o} \qquad (2.2)$$

Where W_s = maximum capacity of a unit weight of the adsorbent for the adsorbate, $\frac{\text{grams adsorbate}}{\text{grams adsorbent}}$

W = weight of adsorbent in the bed, g. Simple mass conservation applied to a typical curve of output concentration vs. elapsed time will readily show that t_s will be found when $C/C_o = 0.5$.

Equation (2.1) is an approximate relation applicable to any adsorbent. However, its validity is limited to a range of elapsed times from perhaps $0.1 < \frac{t}{t_s} < 0.8$, since at $t = t_s$ Equation (2.1) is inconsistent with the definition of t_s in Equation (2.2) [i.e., (2.1) requires $C = C_o$ at t_s]. At $t \ll t_s$ the asymptotic form requires, correctly, that $C \leq C_o$ but it does not describe a definite breakthrough time (i.e., first penetration). Nonetheless, the relation has a simple form and is relevant to field practice since sampling with solid adsorbents must be designed to prevent significant adsorbate loss. The valid range of elapsed times is likely to be particularly relevant to that objective.

Models applied to air sampling have been approached from a conventional chromatographic perspective in the past[1,2]. Hence, equations (2.1) and (2.2) may seem unfamiliar. The following discussion may help to put terms into a more familiar perspective.

If the adsorption of some substance is occurring at equilibrium on some adsorbent then, in general,

$$\Gamma = \int_0^{C_o} \frac{\partial \Gamma}{\partial C}\, dC = W_s W \qquad (2.3)$$

where Γ is the Gibb's surface excess (the amount adsorbed at equilibrium).

Define:

$$\left(\frac{\partial \Gamma}{\partial C}\right)_{T,P,C_i} = V_b \qquad (2.4)$$

Where T is temperature
P is pressure
C_i is a concentration of substance i

If, as is usual, the tube output behavior (concentration vs. time) is symmetric about $C_o/2$ and if Equation (2.3) is integrated assuming V_b is a constant, then

$$\Gamma = V_b C_o = W_s W \qquad (2.5)$$

C_o is the concentration in the gas phase of the substance of interest. Using relation (2.5) in Equation (2.2) yields the familiar

$$t_s = \frac{V_b}{Q} \qquad (2.6)$$

V_b is a parameter with the dimensions of volume, cm^3. It is by definition (2.4) the slope of the equilibrium adsorption isotherm.

Equation (2.6) indicates that under these conditions t_s does not depend on the input concentration [compare with Equation (2.2)]. This independence of input concentration is the one condition which must be met if Equation (2.1) is to be applied to air sampling where concentrations fluctuate. V_b is, of course, the familiar retention volume of chromatography; that is, the volume of fluid which has passed through the bed when the outlet concentration is equal to one-half the inlet concentration. V_b has also sometimes been called the breakthrough volume although this term is often reserved for the point of first penetration of the bed by the adsorbate. V_b is as important a parameter in Equation (2.1) as it is in earlier approaches although Equation (2.1) will not describe the situation at t_s.

In order to meet the mathematical requirement (V_b = a constant) physically, the gaseous solution being sampled must be so dilute that each adsorbate molecule of whatever kind acts independently of all other adsorbate molecules. This is sometimes referred to as being in "the Henry's Law region." V_b certainly depends on the surface condition of the adsorbent, the composition of the gaseous solution, and temperature. Atmospheric pressure is assumed.

V_b is a thermodynamic quantity. If it is determined using chromatography or by computation from the shape of an equilibrium adsorption isotherm it should be applicable in Equation (2.1). However, there is no way at this point either to decide a priori or to extrapolate from limited experience with pure substances or simple mixtures, the concentrations or compositions which define the limits of the Henry's Law region. This is especially true when the fluids of interest are multicomponent gaseous mixtures of uncontrolled and variable composition such as are necessarily dealt with in air sampling.

If V_b is not constant in some situation, use of tabulated retention volumes will be incorrect. If composition or concentration effects happen to be very large or if the temperature changes greatly during sampling and inlet concentrations are fluctuating (as they almost certainly are) even qualitative analyses on samples could be suspect, since some substances collected early in the period might be eluted and not replaced. Evidence in every sampling situation that the relevant V_b had not been exceeded importantly would be vital if Equation (2.1) were applied.

K_o is a kinetic parameter dependent not only on the temperature, pressure, and composition variables but on the fluid mechanic regime and surface geometry/state of the adsorbent, as well. For example, if an "apparent breakthrough volume" (i.e., one obtained for a fixed input composition by direct observation of the volume sampled when the output concentration reached $C_o/2$), appeared to be a function of the total flow rate, it might conceivably be because the adsorbent contained a significant quantity of pores. Because of the possible size distribution of the pores, flow rate increases could cause pore interiors to become increasingly inaccessible for effective entry by the gas above some linear velocity. That part of the surface inside the pores would therefore become progressively unavailable for adsorption at and above certain flow rates.

Although such observations have been reported[4] and have been interpreted reasonably in these terms, rigorous application of this model [Equation (2.1)] would require that V_b be unaltered but K_o become a function of flow rate. Equation (2.1) may even be inadequate because inclusion of additional parameters may be needed to describe such situations. However, K_o is expected to be sensitive to sample geometry and flow rate. Its value cannot be estimated on Tenax at present by any means other than experimentation in a situation which is an exact duplication of the conditions utilized in sampling.

A recent report about solid adsorbent sampling from the chromatographic viewpoint[1] has pointed out the importance of the number of theoretical plates in modeling sampling. K_o in Equation (2.1) is not the number of theoretical plates, but it functions in a similar way though in a form more relevant to practical considerations. The term $(K_o L/V_L)$ in Equation (2.1) can be viewed as a ratio of a superficial residence time in the bed for an inert species L/V_L to a pseudo characteristic adsorption residence time $1/K_o$ for the species of concern. If such a term is adequate for sampling considerations (i.e., K_o is well behaved) fundamental interpretations are improbable but explicit statements of flow and geometric effects would be available for interpolation between the extremes of experimental evidence.

Utilization of this simple mathematical model, should it prove to be adequate, would then permit:

1. An ability, within limits of experimentally observed extremes, to design sampling tubes which will perform as expected during sampling. Dimensional rescaling of the tube and flow rate to yield identical time-output concentration curves could be done.

2. A practical guide to field operations. The model would yield a simple way to calculate the sampling rate if bed geometry, sampling duration, and some idea of the substances of interest exist. These, of course, are the principal sampling variables. If the model proves acceptable, practical ways of dealing with uncontrollable variables (i.e., temperature and composition of the atmosphere and practical limits to knowledge and information) must be provided through suggestions about ways to utilize

the model in any actual sampling situation. The obvious traditional and effective answer is to build a special redundancy into every project.

The model will not permit:

1. Estimation of the sampling efficiency for a substance which has never been observed.

2. Estimation of mechanical and thermal behavior of the cartridges. Pressure drop and pump requirements for sampling and the thermal behavior of the tube in the desorption cycle (quantitative removal of adsorbate) are simply not addressed.

3. Correction of the analytical data if assumed retention volumes are exceeded during sampling.

SECTION 3

EXPERIMENTAL APPROACH

METHOD

A schematic diagram of the experimental apparatus is shown in Figure 1. Clean, dry air was passed over a calibrated permeation tube containing the compound for which the retention volume was to be determined. After exiting the permeation chamber the stream passed through a mixing chamber. Then it was divided and a measured portion was pumped away. The volume of flow thus discarded was adjusted to control the total flow rate through the permeation chamber to fix the concentration of compound in the air stream. The remainder of the stream was drawn through a Tenax sampling cartridge mounted in a temperature controlled chamber. The effluent stream from the cartridge was split and a portion of it was pumped away. The volume of this discarded flow was adjusted to control the flow rate through the cartridge. The small, constant remainder of the flow was drawn through a hydrocarbon analyzer which periodically diverted an aliquot of it into a flame ionization detector (FID). The FID response was monitored on a recorder, resulting in a series of regularly spaced peaks on a strip chart which began to appear at some interval after the beginning of the experiment and increased in height from zero to a maximum value equal to that obtained with no cartridge in line with the flow. The response (fraction of maximum response) corresponding to elution of a given volume of air (liters) was calculated.

EQUIPMENT

Compressed air was passed through an Aadco Model 737 Pure Air Generator equipped with a methane reactor. The output was regulated to 3.8×10^5 Pa gauge (55 psig) by an internal pressure regulator. This pressure was stepped down to 7.6×10^4 Pa gauge (11 psig) by a Fairchild Kendall Model 10 pressure regulator and further stepped down to 1240 Pa (5 in of water) equivalent by a Moore Model 40-2 regulator.

The permeation chamber and the sampling chamber were made of borosilicate glass. A temperature equilibration coil 1 m in length was inside the jacket upstream of the chamber. The mixing chamber was also made from borosilicate glass. Flow lines were 0.32 cm (1/8 in) OD tubing made of 316 stainless steel. Haake Model FE constant temperature circulators in line with refrigeration units were used to supply constant temperature fluid to the sampling and permeation chamber jackets through 1.27 cm (½ in) ID Tygon tubing. The circulating fluid was a 1/1 mixture of ethanol and deionized water.

A Valco 0.32 cm (1/8 in) four-port zero volume valve was used to isolate the sampling chamber while removing and replacing cartridges. Flow rates were controlled with Tylan Model FC-260 and FC-261 mass flow controllers. These were available in nominal ranges of 50, 100, 500, 1000, 5000, 10000, and 20,000 ml/min (air). Each flow controller was calibrated individually by measuring actual flow rate with a Hastings Model HBM-1 bubble meter for a given controller reading. Linear regression of 30 points was used to get the slope and intercept of a plot of flow rate (as measured at 23°C and 60% relative humidity) vs. controller reading. Since the entire apparatus was housed inside a Forma Environmental Chamber, corrections of flows to STP were not made.

Tenax GC sampling cartridges of various bed dimensions were necked down to 0.64 cm (¼ in) at one end so that they could be attached to a 0.64 cm (¼ in) tube fitting with Teflon ferrules. Processing of Tenax and preparation of cartridges was carried out according to the EMSL Standard Operating Procedure (SOP).

A Bendix Model 8201A Hydrocarbon Analyzer was modified for use as a flow line sampler. Since air was being drawn rather than pushed through the sampler, the sample line pressure regulator was removed and its connection to the sample line was capped. In order to read "total hydrocarbon" at each injection the analytical column and backflush valve were bypassed so that each injection of the sample valve went straight to the FID. The output from the FID was recorded on an Esterline-Angus Speed Servo II recorder equipped with a calibrated zero offset. Full scale ranges of 0.5, 1, 5, 10, and 50 mV were used. A KNF Neuberger Model No. 35.3 ANP diaphragm pump was used to draw air through the system.

CHEMICALS

All chemicals used were tested for purity by glass capillary GC with FID. Compounds less than 98% pure were distilled in a Perkin-Elmer Model 251 Auto Annular Still.

Permeation tubes were made from 0.62 cm (¼ in) OD by 4 or 5 μm (~0.0002 in) ID plastic tubing. Three kinds of tubing were used: (1) Polyethylene (PE), (2) Polytetrafluoroethylene Teflon (TFE), and (3) Fluorinated Ethylene and Propylene Teflon (FEP). Tubes were filled with compound and the ends sealed with glass plugs secured by compressing 0.64 cm (¼ in) stainless steel Swagelok ferrules around the plastic with a split nut. Permeation tubes were calibrated by weighing on a Mettler H20 semimicro balance at intervals of one or two weeks and linear regression of the results of the five most recent weighings were used to establish the permeation rate. Permeation tubes were stored and used in glass jacketed chambers maintained at 23°C (73°F) by thermostatically controlled recirculating fluid. Cleaned virgin Tenax from the same lot was used for all tests.

PROCEDURE

Flow controller readings required to produce a specified flow rate through the cartridge and compound concentration were calculated. Then air was drawn through the system with no cartridge or permeation tube in place while the flows were set, and the hydrocarbon analyzer was operated with the recorder on 0.5 mV scale to confirm that clean air was passing through the system. Then the recorder was reset to the scale needed to accommodate the peak heights expected during the experiment and zero readings were taken, if necessary. Zero readings were normally needed only for 0.5 and 1 mV scales and resulted from baseline deflections produced by switching of the sample valve.

After observing the baseline for at least 12 injections the permeation tube was put in line. When peak heights had stabilized (usually in less than 10 injections) the sample chamber was isolated from flow with the four-port valve and the cartridge installed. A minimum of 10 min were allowed for temperature equilibration of the cartridge during which time at least six injections would have occurred while chemical concentration in the flow line was at maximum. Then the four-port valve was switched to bring the cartridge in line with the flow and the chart was marked to indicate beginning of the run. Peak heights rapidly decreased to approximately zero and later began to increase again. Runs were normally terminated only after peak heights had again reached their maximum value.

The total volume of air eluted from the cartridge at a given peak was calculated from elapsed time (read from the chart) and the flow rate. Peak height (corrected for zero, if necessary) was divided by maximum peak height (similarly corrected) to give the fraction of maximum concentration.

SECTION 4

MODEL TESTING

The utility of the model was tested in two ways:

1. A test of agreement of retention volumes with published Research Triangle Institute (RTI) values([5]) was undertaken. Sampling was simulated using a permeation tube system. Flame ionization detection of the output of the Tenax cartridge was utilized to obtain a relationship between an elapsed time and the concentration of the pollutant in the effluent from the cartridge. With few exceptions, only single substances were used at one time. The flowing fluid was cleaned air. Sampling tubes and flow rates were fixed at those that had been utilized in the field previously. As a laboratory expedient, concentrations were higher than are usually found in the field, but the effects of changes in concentration and temperature were investigated.

2. Independent manipulation of other variables was undertaken. Within practical limits temperatures and pollutant concentrations were fixed but tube geometry and flow rates were varied. The purpose of this work was to investigate the behavior of the adjustable constants in Equation (2.1) when other parameters were manipulated independently.

Each test will be discussed in turn.

RELATIONSHIP TO PUBLISHED RETENTION VOLUMES, THE FIRST SET OF TESTS

Procedure and Results

The objectives of these experiments were to relate our experimental data to the information on "breakthrough volumes" previously published by RTI([5]) and to assess the adherance to Henry's Law at these concentrations.

To establish these relationships pure air was doped with chloroform, trichloroethylene, benzene, or tetrachloroethylene and passed through a Tenax cartridge of the design usually used in the field (1.2 g Tenax in a bed 1.25 cm in diameter and 6 cm long). The flow rate was 300 ml/min, the same as usually used in the field at that time. The effluent stream from the cartridge was periodically monitored about every 100 s using the flame ionization detector. Resulting data consisted of output stream concentrations at various elapsed times. The inlet concentration of the given substance and the Tenax temperature were the principal variables in this work. Four experiments, however, were done where interactions between chemicals on the Tenax were observed (see Table I).

The relationship to RTI's data was established as follows: Equation (2.1) can be rewritten as:

$$\frac{t}{t_s} = 1 + \frac{V_L}{K_o L} \ln \frac{C}{C_o} = t_r \qquad (4.1.1)$$

$\frac{t}{t_s}$ was calculated using the RTI value ($t_s = V_b/Q$). Then a table of $\frac{t}{t_s}$ vs. $\ln \frac{C}{C_o}$ was produced from the raw data of each experiment.

Each set of data was then subjected to a standard linear least squares procedure, where y was taken as t_r to obtain a slope and an intercept which can be identified with the terms in the model [Equation (4.1.1)]. Thus:

$$t_r = I + S \ln \frac{C}{C_o} \qquad (4.1.2)$$

The results of the experiments are summarized in Table I. The empirical values of slopes and intercepts have been determined only from data in the range of $0.2 < t_r < 0.8$. A calculated reduced retention time and an observed one are recorded as well as a calculated reduced time for 10% leakage, $t_{.01}$. Calculated times were obtained from the empirical fits using concentration ratios of 0.5 for the retention time and 0.1 for 10% leakage.

Discussion

The interpretation of these data is as follows:

1. The empirical intercept can be identified as the ratio of retention volumes, V_{EMSL}/V_{RTI}. An intercept of exactly 1.00 indicates perfect agreement between the EMSL and the RTI values. RTI values were determined independently and in a different way. Values differing from 1.00 in both directions are possible and indicate an EMSL value either larger or smaller than that published by RTI.

2. Intercepts which change in a monotonic fashion with concentration imply that the observation is not in "the Henry's Law region" of the adsorption isotherm.

3. The slopes can be identified with the coefficient of the logarithmic term in Equation (4.1.1). No comparable information has been published previously.

Clear concentration effects on retention volumes are not apparent at 38°C (100°F). The possibility of some effect exists for the two chlorinated ethylenes because of the lowest concentration results in each case. However, the data are too few in number to be definitive.

It is unequivocal, however, that in the case of chloroform and benzene the added presence of a large quantity of tetrachloroethylene had no effect on the retention volumes of the benzene and the chloroform. Henry's Law seems to hold at this temperature and these (high) concentrations.

All substances have values of the intercepts which are near 1 at 38°C (100°F). This implies reasonable agreement with the published RTI values of retention volumes. The agreement, generally within about 25%, is excellent since in other published comparisons between different laboratories agreement has sometimes been only within a factor of ten([6]).

The observed slopes at 38°C (100°F) appear to be independent of concentration except perhaps at the very lowest concentrations for all substances tested. If the lowest concentration is ignored the range of the data is still large. However, large variability in rate constants from these kinds of measurements is not unusual. This variability is probably of little practical importance for sampling. Much more investigation would be necessary to understand these effects more thoroughly.

At 10°C (50°F) the slopes cannot be compared with a standard since there is no published information. It appears that there is a concentration dependence in all cases. However, the data are not sufficient to make this certain. The large range of slopes is unimportant for present objectives.

At 10°C (50°F) the concentration dependence of the intercept is clear in every case, although tetrachloroethylene is somewhat equivocal because of the existence of only two values. This concentration dependence implies that at this lower temperature and these concentrations, which are the same as those used at 38°C (100°F), Henry's Law has been violated. Also consistent with this interpretation is a major effect (reduction) on the retention volume observed in both cases where challenge with tetrachloroethylene was tried.

These observations indicate that a well-behaved system at one temperature does not imply that the system will be equally well behaved at another temperature both of which will on occasion be observed in field sampling. However, disagreement with the published RTI values at 10°C (50°F) is again smaller than a factor of 10. Disagreement is in a direction that should not cause sampling based on these literature values to be faulty.

The objection might be raised that concentrations such as those used here are unrealistically large for ambient work. They were, regrettably, the lowest permitted by experimental limitations. However, results of some experiments in the field are available which bear on this objection. (Parts per billion are ambiguous, equivocal, and undesirable units although they are employed rather commonly in atmospheric work. For present purposes, ppb is defined as $\sim 10^{-9}$ g/l of air.) If 25ℓ of air with a 400 ppb impurity (a typical concentration at which many of the experiments were performed)

are sampled with 100% collection efficiency, the amount of material adsorbed on the tube would be 10^4 ng or about 4×10^5 ng/m^3 of air. The analytical data in Table V produced from tubes exposed to ambient air at a location in Houston, Texas indicate values for some of these selected substances approaching 400 ppb[7]. These data were rounded to give only one significant figure. There are many other substances in these atmospheric samples, many more than were ever involved in laboratory experiments. These other substances were not quantitated and do not appear in the tables. Therefore, real samples have been collected with concentrations approaching those used in the laboratory.

It is not possible to calculate, or to predict, the effect of complex mixtures on the retention volume of any individual substance given the present state of knowledge. However, since some values have been reported based on field experience with real ambient samples and those values approach the concentrations in tubes where Henry's Law violations have been observed in simpler situations in the laboratory, it would be unwise to ignore the possibility that Henry's Law can be violated in field sampling. Indeed, if it were violated it would be in precisely those situations which would be of most concern to the U. S. Environmental Protection Agency.

It is noteworthy that the retention times computed in this work were fits of a parameter obtained from data that did not include the direct observation of the retention volume. Elapsed times greater than t_s were experimentally observed in this work. Retention volumes were interpolated from observation in an approximate fashion. Table I also contains a ratio of the approximate observed retention volume from this work to that reported by RTI. The agreement is reasonable, in all cases, with the ratio computed from the fit of the model.

The reduced time to obtain a leakage of 10% of the input concentration, t_{01}, has also been computed from the model. The general conclusion for all substances is that this rate of leakage occurs at about one-half of the observed retention volume; this fact will be utilized below in making suggestions for sampling computations.

In summary, the model verifies published retention volumes within reasonable limits. This agreement strengthens the credibility of the model since a derived indirect result compares favorably with one determined more directly.

EFFECTS OF CHANGES IN GEOMETRY AND FLOW RATE, THE SECOND SET OF TESTS

Procedure and Results

In the second set of experiments the temperature of the Tenax was fixed at 38°C (100°F), the highest usual operating ambient temperature which might routinely be expected. (Retention volumes diminish with increasing temperature. Therefore, a practical advantage of operating at

this single temperature was the minimization of the duration of experiment.) Concentrations in these tests were held to less than 50 ppb (except for chloroform for which the FID detector response was inadequate below 150 ppb). Experiments were done in the same fashion with the same equipment used in the first tests except that cartridge dimensions and flow rates were altered independently and over as wide a range as practical.

The data consist of tables of liters of air passed through the cartridge versus concentration of the eluting pollutant. These data were converted to cubic centimeters of air vs. ln C/C_o and were then subjected to a least squares fit (y = cc of air). The relevant volumetric (time) range for which the model is valid was observed closely.

The objective was to examine the constancy of the adjustable parameters in the model (V_b, K_o) given the arbitrary manipulation of the other independent parameters. Again this was effected by computation of the retention volume and K_o from the constants of the empirical fits through the following scheme of identification:

Rewriting Equation (2.1) as

$$t = t_s\left[1 + \frac{V_L}{K_o L} \ln \frac{C}{C_o}\right] \qquad (4.2.1\text{-}1)$$

Substitute Equation (2.2)

$$= \frac{W_s}{QC_o}\left[W + \frac{WV_L}{K_o L} \ln \frac{C}{C_o}\right] \qquad (4.2.1\text{-}2)$$

Rearrange and substitute Equation (2.1-A):

$$tQ = \frac{W_s}{C_o}\left[W + \frac{WQ}{\pi K_o R^2 L} \ln \frac{C}{C_o}\right] \qquad (4.2.1\text{-}3)$$

tQ = volume of air sampled = y in the least squares fit.

Identify the least squares constants, intercept and slope, with adjustable parameters as follows:

$$\text{intercept} = \frac{W_s W}{C_o} = V_b$$

$$K_o = \frac{(\text{intercept})\ Q}{(\text{slope})\ \pi R^2 L}$$

Table II contains values of independent variables selected, empirical constants, and parameters derived from the second set of tests. The same information about the average results from the first set of tests at 38°C (100°F) has also been included.

Discussion

The most extensive series of experiments in this portion of the study utilized toluene. The retention volumes bear no discernable functional relationship to independent variables and are clustered within 25% of the mean value. This suggests that retention volume measurements are reasonable.

All but two of the substances have retention volumes that are within about 25% of published values([5]). None exhibit any obvious functional dependence in spite of the wide range of flow rates and tube geometries. (Recall that all input concentrations in these experiments were less than 50 ppb except for chloroform which was 150 ppb. These values are substantially smaller than most of those used in the previous work where the range was 50 to 5000 ppb.)

The K_o values exhibit a great deal of variability. A dependence of K_o on linear velocity is apparent for toluene (velocity = 73.4 + .627 K_o, ρ = 0.93). This relationship then indicates a tendency of the entire pre-exponential term in Equation (2.1) to be constant. However, that is not the case for benzene (velocity = 37.7 + .478 K_o, ρ = 0.58). This data set is then too small to be conclusive or to permit interpretation in terms of any more fundamental models.

Examining values of K_o in Table II for all substances as a group, and ignoring functional dependence where it exists, shows that all but two values lie between 30 and 400 with a typical value of $\sim$ 200. The two values outside of this range (which are replicates) are both cases where the superficial linear velocity is significantly higher than in all other cases. The higher K_o value suggests a slower leakage of material from the tube than would be apparent using the value of 200. These results might be due to experimental difficulties in switching the cartridges in and out of the line in the permeation system. However, additional and different experiments would be required to ascertain the causes. For present purposes these data are considered adequate.

SECTION 5

CONCLUSIONS

The available evidence is not inconsistent with the proposed model. The model is capable of giving a reasonable and compact description of the sampling behavior of the Tenax cartridges over a range of variables likely to be met in the field. The data are neither sufficiently extensive nor designed to permit a critical evaluation of the model by invoking attempts to calculate or scale the adjustable parameters using even more fundamental information or a reduced relationship approach. Extrapolation of the model beyond the limits of experimental evidence is uncertain.

SECTION 6

UTILIZATION OF THE MODEL FOR ROUTINE SAMPLING

In using the model for guidance in field sampling a number of needs must be met simultaneously. Serious information gaps exist. Absence of knowledge about the behavior of retention volumes if not to be filled in by assumptions of questionable or untestable validality, are very significant. And finally, the practical limitations of economy and simplicity imposed by routine application by many operators over a wide geographic area impose severe restrictions.

An attempt has been made in Table III to set out in succinct form some needs, their technical implications, some uncertainties or limitations, and a conclusion or response.

The contents of Table III suggest the appropriateness of the application of a single conservative limiting relationship to design sampling and the need for redundancy.

The suggested general approach for the routine situation is as follows:

1. Use a fixed cartridge size. (At present GC/MS sample desorbers limit severely the options with respect to cartridge size.)

2. Allow the single substance, whose determination is required and which is expected to have the smallest retention volume at one arbitrary high temperature based on published information, control the sampling calculations. If necessary, divide the list into ranges of retention volumes and sample independently for each range.

3. The desired sample averaging time will be specified by the situation.

4. Compute a flow rate conservatively using the model. If ambient temperatures are expected to be cool, use the computed value. If temperatures are near 29°C (85°F) or higher, use one-half the computed value.

5. Provide evidence of the data credibility. Take a duplicate for every sample in parallel but at a different flow rate (e.g., the one computed in 4 above and another at one-half of that value). "Agreement" of the analyses on duplicate samples would be an indication of adequate retention. Therefore, while two analyses must be done, each analysis gives "complete" information. Comparison provides quality assurance information. By providing data evaluation this approach is more "efficient" than

the tandem tube approach which requires the same resources but also depends on assumptions and provides no basis for evaluation.

Even with these precautions other factors must be considered in data evaluation. Artifact formation can occur on the Tenax. To check whether some species is an artifact, comparison of data from two different adsorbents in addition to two different flow rates might be suggestive. Results would depend on the mechanisms of formation of the artifacts. A completely different technique would be better for testing this possibility.

Also, even though analytical agreement might exist for duplicate samples, this does not provide evidence for accuracy of the results. Significant analytical biases can exist for reasons which have nothing to do with sampling. Precise results can be very inaccurate. Disagreement between analyses on two duplicate samples would indicate difficulties of some sort, but it is unlikely that an identification of the problem could succeed. Moreover, the data could not be corrected.

Common sense, caution, and redundancy must be employed to insure that large air volumes sampled do not overload the GC/MS with excessive quantities of adequately retained materials but that samples are large enough to be above detection limits.

SECTION 7

UTILIZATION OF THE MODEL FOR SAMPLE TUBE DESIGN

If the flow rates fall outside of the range for which the model was tested, then: (1) the sampling time must be redefined, (2) the required substances changed or divided into more groups, or (3) a new cartridge must be designed for the particular purpose. The first two possibilities will not be discussed here. Rather, a tube design approach is suggested.

Sampling tube dimensions are critical for thermal desorption with existing equipment. Before any new tube size is employed its compatibility with desorption equipment must be assured.

A rational design procedure might be as follows: (symbols have the same meaning listed in Section 2).

1. Pick a flow rate in the acceptable range (10 to 400 cm^3/min) and compute a Tenax weight in grams using the relevant retention volume per gram of Tenax.

$$W = \frac{Qt}{V_b} \qquad (7.1)$$

2. Compute the bed volume using the weight from (7.1) in Equation (7.2).

$$V = \frac{W}{0.16} \qquad (7.2)$$

3. Compute a bed length by assuming a radius somewhere in the range of 0.6-1.25 cm using the volume obtained from Equation (7.2). Check the following relations to be sure they are satisfied:

$$1.25 > R > 0.6 \qquad (7.3)$$

$$2 < L/R < 4 \qquad (7.4)$$

$$30 < \frac{Q}{\pi R^2} < 400 \qquad (7.5)$$

Go back through this procedure and adjust iteratively until all constraints (7.3-7.5) are met. If any constraints cannot be met then extrapolation of the model beyond present experience will be required. This may be workable but should be done with great caution.

It will be essential to check with analysts to assure compatibility of the cartridge with laboratory equipment. Moreover, it may be necessary to experiment with the cartridge to assure that the pumps on the sampler are adequate.

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TABLE I
First Set of Tests
Reduced Sampling Equations
$t_r = I + S \ln C/C_o$

Substance	Conc in ppb	Temp °F	Intercept, I	Slope, S	Reduced Retention Time Observed	Reduced Retention Time Calculated	$t_{0.1}$ Calculated	Comments
Chloroform	100	50	2.611	1.103	1.8	1.9	0.1	
	100	100	0.987	0.722	---	0.5	<0	
	490	50	2.264	0.530	2.3	1.9	1	
	490	50	1.278	0.281	---	1.1	0.6	Challenge with 2100 ppb C_2Cl_4
	490	100	0.987	0.297	0.79	0.77	0.3	
	490	100	0.931	0.361	---	0.7	0.1	Challenge with 2100 ppb C_2Cl_4
	490	100	0.859	0.200	0.7	0.8	0.4	(35 ml/min flow)
	5900	50	1.522	0.304	1.5	1.3	0.8	
	5900	100	0.816	0.232	0.68	0.66	0.3	
	19000	50	1.081	0.221	~1	0.9	0.6	
	19000	100	0.861	0.164	0.73	0.75	0.5	
Trichloro-	90	50	3.137	1.058	3.7	2.4	0.7	
ethylene	90	100	1.301	0.617	1	0.9	<0	
	790	50	2.978	0.573	3	2.6	1.7	
	780	100	0.973	0.223	0.9	0.8	0.5	
	1900	50	2.156	0.393	2.1	1.9	1.3	
	1900	100	0.995	0.217	1.2	0.9	0.5	
	5000	100	0.899	0.179	1	0.8	0.5	
Benzene	30	50	2.881	0.791	2.4	2.3	1.1	
	30	100	1.250	0.374	1	1	0.4	
	260	50	1.958	0.464	2.1	1.6	0.9	
	260	50	1.106	0.243	---	0.9	0.5	Challenge with 2100 ppb C_2Cl_4
	260	100	1.014	0.233	1	0.9	0.5	
	260	100	1.127	0.302	-	0.9	0.4	Challenge with 2100 ppb C_2Cl_4
	260	100	1.186	0.161	1.2	1.1	0.8	(35 ml/min flow)
	590	50	1.560	0.280	1.6	1.4	0.9	
	670	100	0.977	0.253	0.97	0.8	0.4	
	5100	50	0.834	0.124	0.8	0.8	0.5	
	5000	100	0.915	0.160	0.94	0.8	0.6	
Tetrachloro-	60	50	2.906	0.641	---	2.5	1.4	
ethylene	60	100	1.574	0.446	1.3	1.3	0.6	
	170	50	2.727	0.671	---	2.3	1.2	
	170	100	1.123	0.291	1.2	0.9	0.5	
	600	100	1.105	0.219	1.2	1	0.6	
	2100	100	1.013	0.219	1.2	0.8	0.3	

TABLE II
Second Set of Tests
Derived Parameters

Bed Length, cm	Bed Diameter, cm	Volume Flow Rate, cm^3/min	Linear Vel., cm/min	Tenax mass, g	Intercept, cm^3	Slope, cm^3	Correl. Coeff.	Ret. Vol, ℓ/g	K°, min^{-1}	Comments
				Toluene (RTI V_b = 72 ℓ/g)						
6	0.6	100	350	0.28	30060	6700	0.93	107	260	
6	0.6	100	350	0.28	27560	4070	0.98	98	400	
6	0.6	35	120	0.27	27520	2120	0.98	102	270	
6	0.6	35	120	0.25	25030	1840	0.92	100	280	
6	1.25	500	400	1.20	94180	26380	0.83	78	250	
6	1.25	300	240	1.15	104300	29780	0.80	91	150	
6	1.25	100	80	1.14	130700	35150	0.98	115	50	
2.2	1.25	300	240	0.41	35510	10550	0.96	87	380	
2.2	1.25	100	80	0.43	40900	13130	0.90	95	120	
2.2	1.25	35	30	0.39	46700	12670	0.94	120	50	
2.2	0.6	300	1100	0.12	10710	4310	0.99	89	1200	
2.2	0.6	300	1100	0.13	9430	2420	0.97	73	1900	
				Benzene (RTI V_b = 16 ℓ/g)						
2.2	1.25	300	240	0.43	5940	1860	0.97	15	360	
2.2	1.25	35	30	0.43	8110	2430	0.99	19	40	
2.2	0.6	35	120	0.13	2790	1260	0.95	21	120	
6	1.25	35	30	1.16	20070	2730	0.96	17	40	
6	1.25	300	240	(1.2)*				16	160	(Avg. from Table I)
6	1.25	35	30	(1.2)				19	250	(From Table I)
				Chloroform (RTI V_b = 8 ℓ/g)						
6	0.6	100	350	0.27	2050	654	0.99	8	190	
6	1.25	300	240	(1.2)				7	110	(Avg. from Table I)
6	1.25	35	30	(1.2)				7	200	(From Table I)
				Trichloroethylene (RTI V_b = 18 ℓ/g)						
6	1.25	300	240	(1.2)				18	130	(Avg. from Table I)
				Tetrachloroethylene (RTI V_b = 65 ℓ/g)						
6	1.25	300	240	(1.2)				80	130	(Avg. from Table I)
				1,2-Dichloroethane (RTI V_b = 12 ℓ/g)						
6	1.25	300	240	(1.2)	7570	2900	0.88	6	110	
				1,3-Dichloropropane (RTI V_b = 60 ℓ/g)						
6	1.25	300	240	1.14	106600	49800	0.96	94	90	

*Mass estimated not measured

TABLE III

Summary of Considerations

Need	Technical Implications	Limitations/Uncertainties	Response
Simplicity / Reliability / Minimum Cost.	One standard procedure for all cases. Minimum no. judgments, assumptions and variables.	Optimization problem; knowledge/info limitations.	Base SOP on one set of conservative limiting assumptions.
Apply SOP Now.	State of art.	State is primitive.	---
Calculate sampling rates easily to facilitate rational field operation.	Relation between averaging time, flow rate, breakthrough and Tenax geometry.	Behavior and knowledge about parameters meagre. Theory about behavior not predictive.	Adopt limiting case for model.
Assure and demonstrate adequate pollutant capture during sampling.	Demonstrate possibility of capture and improbability of formation as artifact.	Theory can't help. Arbitrarily large number of experiments required.	Do every sampling in duplicate (parallel) using two different adsorbents.
	Avoid significant breakthrough.	Retention volumes needed for every substance. Henry's Law demonstrated for each field sample. Theory not predictive. Tandem (series) cartridges conceptually inadequate/or resource intensive.	Do every sampling in duplicate (parallel) using two different flow rates.
Lowest practical detection limit.	Sample largest possible air volume.	Detailed calculation impossible/ impractical.	Adopt limiting case. Try to remove molecules with small V_b from consideration or sample for them separately.
Defensible laboratory results.	Minimize the number of assumptions in the calculations. Demonstrate consistency in each case.	Breakthrough uncertain because of: 1. Variable input concentration and mix 2. Variable temperature 3. Henry's Law validity	Duplicate (parallel) results at differing flow rates and preferably differing adsorbents in every case.

TABLE IV
Approximate Retention Volumes at 38°C (100°F)
ℓ/g of Tenax)

Chemical Class	Species Name	Retention Volume
Halogenated hydrocarbon	methyl chloride	2
	methyl bromide	0.8
	vinyl chloride	0.5
	methylene chloride	2
	chloroform	8
	carbon tetrachloride	8
	1,2-dichloroethane	10
	1,1,1-trichloroethane	6
	tetrachloroethylene	80
	trichloroethylene	20
	1-chloro-2-methylpropene	6
	3-chloro-2-methylpropene	7
	1,2-dichloropropane	30
	1,3-dichloropropane	90
	epichlorohydrin (1-chloro-2,3-epoxypropane)	30
	3-chloro-1-butene	5
	ally chloride	4
	4-chloro-1-butene	10
	1-chloro-2-butene	20
	chlorobenzene	150
	O-dichlorobenzene	300
	m-dichlorobenzene	400
	benzyl chloride	500
	bromoform	100
	ethylene dibromide	60
	bromobenzene	300
Halogenated ethers	2-chloroethyl ethyl ether	70
	Bis-(chloromethyl) ether	120
Nitrosamines	N-nitrosodimethylamine	90
	N-nitrosodiethylamine	420
Oxygenated hydrocarbons	acrolein	3
	glycidaldehyde	40
	butadiene diepoxide	210
	cyclohexene oxide	330
	styrene oxide	930
	phenol	330
	B-propiolactone	100
Nitrogenous hydrocarbons	nitromethane	9
Sulfur compounds	diethyl sulfate	7
	ethyl methane sulfate	830

TABLE IV (Cont'd)
Approximate Retention Volumes at 38°C (100°F)
ℓ/g of Tenax)

Chemical Class	Species Name	Retention Volume
Amines	dimethylamine	0.8
	isobutylamine	9
	t-butylamine	0.8
	di-(n-butyl)amine	1200
	pyridine	56
	aniline	1000
Ethers	diethyl ether	4
	propylene oxide	3
Esters	ethyl acetate	20
	methyl acrylate	20
	methyl methacrylate	70
Ketones	acetone	3
	methyl ethyl ketone	10
	methyl vinyl ketone	10
	acetophenone	860
Aldehydes	acetaldehyde	0.6
	benzaldehyde	920
Alcohols	methanol	0.3
	n-propanol	4
	allyl alcohol	5
Aromatics	benzene	19
	toluene	97
	ethylbenzene	200
	cumene	440
Hydrocarbons	n-hexane	5
	n-heptane	20
	1-hexene	5
	1-heptene	40
	2,2-dimethylbutane	0.1
	2,4-dimethylpentane	20
	4-methyl-1-pentene	3
	cyclohexane	8

TABLE V

ESTIMATED LEVELS OF VAPOR-PHASE ORGANICS IN AMBIENT AIR[a]
HOUSTON, TEXAS

Substance/Sample ID	T1155	T1255	T1355	T1245	T1345	T1124	T1224	T1324	T1214	T1314	T3365	T4114	T4334	Blank[c]
1,1,1-Trichloroethane	7000	5000	6000	6000	6000	10000	10000	7000	20000	10000	4000	300	100	6
Benzene	150000	70000	70000	10000	60000	70000	120000	110000	90000	50000	30000	2000	2000	127
Trichloroethylene	2000	1000	1000	1000	1000	9000	8000	2000	10000	5000	2000	600	100	50
Toluene	90000	60000	100000	40000	30000	90000	900000	100000	80000	70000	40000	8000	6000	170
Tetrachloroethylene	400	200	300	300	200	2000	2000	900	1000	b	400	700	200	T
Chlorobenzene	100	200	100	50	90	400	400	300	5000	b	200	200	100	3
Xylenes	60000	40000	80000	7000	10000	40000	70000	60000	40000	b	30000	7000	5000	17
Ethylbenzene	10000	8000	10000	1000	2000	7000	20000	10000	7000	b	4000	1000	800	5

[a] Values in ng/m^3.

[b] Data lost due to instrument malfunction.

[c] Values in ng/cartridge, background subtracted from samples.

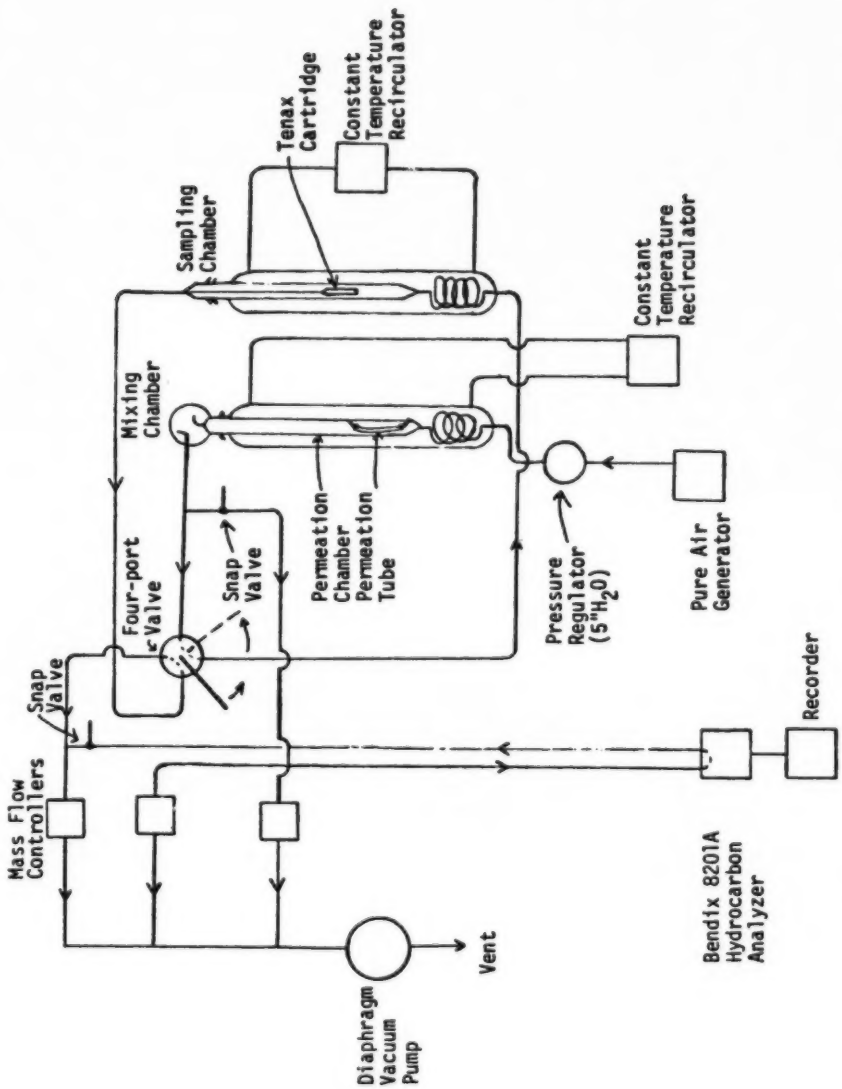

Figure 1. Flow system for measuring elution of organic vapor from a Tenax cartridge.